



Substitute Specification

Title: Programmable Metallization Cell Memory with
Multiple Extra-Small Resistive elements ~~FABRICATION~~
~~OF ULTRA-SMALL MEMORY ELEMENTS~~

Cross-reference to related applications: This application
claims the benefit of PPA # 60/394,139, filed by 07/05/2002
by the present inventor

Federally sponsored research: none

FIELD OF THE INVENTION

001 The present invention relates generally to
~~semiconductor fabricating techniques, and more particularly~~
~~to a method to make ultra-small size memory element such~~
~~as, for example, phase change resistive memory and the~~
structure of programming metallization cell memory (PMCm)
and its fabrication.

THE BACKGROUND OF THE INVENTION

002 ~~In the recent years, a great deal of effort has been devoted to develop various non-volatile resistive memories. Generally, this kind of memory consists of a resistive element which is located between two electrodes. The resistive element can switch in different resistance values (or states) by a programming pulse current to realize the storage of the information. Two typical memories of using the resistive element to store the information are the electrically erasable phase change memory (herein we call it phase change memory) and programming metallization cell memory (PMCm). In both of these memories, the resistive element material is made by filling resistive element material in an opening which is normally formed in a dielectric layer, while the dielectric layer is sandwiched in the electrodes. The resistive element contacts with the electrodes and constitutes a resistor. After the programming current flows through the resistive element, the resistance of the resistive element is changed and thus the information is stored. The PMCm is a kind of non-volatile memory using programmable metallization cell (PMC) to store the information (US Patent No. 6,348,365). A PMC comprises a solid electrolyte and a metal elements contacting to a pair of electrodes. The metallic ions from the metal layer can enter the solid~~

electrolyte resistive element under the certain electric field produced by the programming pulse current or voltage. It results in a change of the resistance of the solid electrolyte element and realizes the information storage. Solid electrolyte element is a key part in PMCM and determines the resistance of the memory. To make solid electrolyte element, an opening is normally first formed in a proper layer, usually a dielectric layer. Then the solid electrolyte is filled in the opening. After that, a thin metallic layer is formed on the solid electrolyte resistive element. Bigger the solid electrolyte resistive element, higher the programming energy is needed for the information storage.

003 ~~In the phase-change memory, the resistive element is made of phase-change material. A typical of phase-change memory is chalcogenide phase-change memory which uses chalcogenide semiconductor as resistive element material (U.S. Pat. No. 3,530,441). The resistance value of the memory switches through the different atomic configuration in the resistive element, from the high resistance in a generally amorphous to a low resistance in a generally crystalline state, while the atomic configuration of the resistive element was changed by the heating effect from~~

~~the programming pulse current. Therefore, the programming energy is directly proportional to the volume of the resistive element or the phase change material.~~

004 ~~The PMCM memory uses the solid electrolyte to make resistive element (US Patent No. 6,348,365). An opening is first formed in a proper layer, usually a dielectric layer. Then the solid electrolyte is filled in the opening. After that, a thin metallic layer is formed on the solid electrolyte resistive element. The metallic ions from the metal layer can enter the solid electrolyte resistive element under the certain electric field produced by the programming pulse current. It results in a change of the resistance of the solid electrolyte resistive element and realizes the information storage. Bigger the solid electrolyte resistive element, higher the programming energy is needed for the information storage.~~

005 To reduce the programming energy of the memory ~~these memories~~, it is desired that the size of the solid electrolyte resistive element be as small as possible. ~~The reduction of size of the resistive element is significant to reducing the programming energy of the memory.~~
~~Considering a phase change memory with a cubic resistive~~

~~element, if the resistive element size is decreased 10~~
~~times smaller, then the volume of the resistive element~~
~~will be 1000 times smaller. For example, if the resistive~~
~~element decreases from the 0.2 μm (2000 \AA) to 0.02 μm (200~~
 ~~\AA), then the volume of the resistive element decreases from~~
 ~~$8 \times 10^{-3} \mu\text{m}^3$ to $8 \times 10^{-6} \mu\text{m}^3$. And it is also meant that the energy~~
~~needed to program a memory will be also approximately 1000~~
~~times smaller. The advantage of decreasing the resistive~~
~~element size is not only the decrease of the programming~~
~~energy, but also that making much faster and higher density~~
~~memory becomes possible.~~

~~006 — The advantage of decreasing the resistive element~~
~~size is not only the decrease of the programming energy,~~
~~but also that making much faster and higher density memory~~
~~becomes possible. Therefore, reduction of the resistive~~
~~element size is a key for resistive memory to become a~~
~~universal non-volatile memory and a potential candidate to~~
~~replace the memories currently extensively used in the~~
~~computer and telecommunication.~~

007 ~~Since the resistive element is normally formed by~~
~~filling the resistive element material in the opening of~~
~~the dielectric layer which is sandwiched in a pair of~~

~~electrodes, the size of the resistive element is essentially determined by the size of the opening. Therefore, to reduce the size of the resistive element essentially means to reduce the size of the opening. Currently, the opening is usually formed by the photolithography and etching processes. The reduction of opening size is limited by the resolution of the photolithography process. The typical minimum opening size that can be obtained by the current photolithography technique is in sub-micrometer, e.g., about 0.2 μm . This size basically determines the minimum resistive element size that can be achieved so far by the conventional photolithography and etching processes.~~

008 ~~For the smaller resistive element size, some special techniques are needed. For example, in the U.S. Patent No. 6,391,688 to Fernando, et al, it was reported that a very small opening with size from 50 to 500 \AA can be made through some special thin film depositions and photolithography processes. But this method includes many processes and may cause high cost, difficulties to control the processes and may also result in low yield.~~

009 It is well known that when two ~~different and~~ unmixable materials are co-deposited onto a substrate, they normally form a composite-phase thin film with two separated phases containing each material. Herein that the two materials are unmixable means that these two materials are not soluble to each other and do not form an alloy containing these materials. In some cases, one material may form the extra-small particles embedded in another material, such as in the case of Fe/SiO₂ composite thin film (J. Applied Physics, Vol **84**, 1998, p5693). Herein we call this particle as nano-dot particle because it has a size in the order of nanometer ($1\text{ nm}=10^{-9}\text{ m}=10\text{ \AA}$). In the present invention, we use this technique to fabricate PMCm memory with multiple extra-small solid electrolyte element.~~ultra-small opening for filling resistive element material to make ultra small resistive element for the memory application.~~ The method of present invention is relatively simple and low-cost to make ultra small memory elements due to avoiding some complicated photolithography processes.

SUMMARY OF THE INVENTION

010 An object of the present invention is to provide a new PMCm memory structure with extremely small solid

electrolyte elements. ~~a new method to make ultra-small opening for the resistive memory element.~~ It is also an object of the present invention to provide a method to make this memory structure ~~memory element with extra-small resistive element.~~ This and other objects of present invention are accomplished by first making a composite-phase thin film with nano-dot particles embedded in a high resistive matrix layer. The materials of the nano-dot particle and high resistive matrix are chosen such that nano-dot particle is active chemically, while the high resistive matrix material is inactive chemically to some chemical or chemical solution. So the nano-dot particle can be etched away by the selected chemicals. The etching can be wet etching or dry etching. A nano-size opening was formed in the position of the particle after the particle was etched away. This opening can be then filled by the corresponding resistive material to make extra-small resistive element. The extremely small size of the solid electrolyte element makes this memory have a good scalability and possibility to make high density memory.

011 ~~Since the resistive element made by the method of present invention can be as small as in nanometer scale, an ultra-low energy can heat such a resistive element to a~~

~~very high temperature. Therefore, for the phase change memory, the resistive element material is not necessary to be limited to some low melting point materials such as chalcogenide semiconductors. Some metals or alloys may be also used as resistive element material.~~

BRIEF DESCRIPTION OF THE DRAWINGS

~~FIG. 1 is a cross sectional view illustrating a phase change memory element with one resistive element layer made by the method of present invention.~~ is a cross sectional view of PMCM memory with multiple solid electrolyte elements.

~~FIG. 2 is a cross sectional view illustrating first electrode and composite phase layer.~~ is a simplified and enlarged perspective view illustrating the structure of composite-phase thin film.

~~FIG. 3 is a simplified and enlarged perspective view illustrating the structure of composite phase thin film.~~ is a cross sectional view illustrating bottom electrode and composite-phase layer after the nano-dot particles were

etched away. An opening was formed after the particle was etched.

~~FIG. 4 is a cross sectional view illustrating first electrode and composite phase layer after the nano-dot particles were etched away. An opening was formed after the particle was etched.~~ is a cross sectional view illustrating the memory structure after solid electrolyte material was filled in the opening.

~~FIG. 5 is a cross sectional view illustrating the memory structure after the phase-change resistive material was filled in the opening.~~ shows ion mill process with ion beam perpendicular to layer surface to form a recession of solid electrolyte element from the matrix layer surface.

~~FIG. 6 shows ion mill process with some incident angle with resistive layer surface to mill away the resistive element material over the matrix layer.~~ is a cross sectional view illustrating a PMCM memory cell with lamination of resistive element, metal and conductive layers.

~~FIG. 7 is a cross sectional view of the memory element after the resistive material over the matrix layer was milled away by the incident ion beam.~~

~~FIG. 8 is a cross sectional view of the PMCM memory after solid electrolyte material was filled in the opening and planerization by ion mill.~~

~~FIG. 9 shows ion mill process with ion beam perpendicular to layer surface to form a recession of solid electrolyte element from the matrix layer surface.~~

~~FIG. 10 is a cross sectional view of the PMCM memory after solid electrolyte resistive element forms a recession from the top surface of the matrix layer by the ion mill with ion beam perpendicular to the layer surface.~~

~~FIG. 11 is a cross sectional view of PMCM memory after the metallic layer was formed on the solid electrolyte element.~~

~~FIG. 12 is a cross sectional view of PMCM memory after top electrode layer and address line was formed.~~

~~FIG. 13 is a cross sectional view illustrating a phase-change memory cell with lamination of ultra-small resistive element layer and conductive layer.~~

~~FIG. 14 is a cross sectional view illustrating a PMCM memory cell with lamination of ultra-small resistive element layer and conductive layer.~~

~~FIG. 15 is a simplified and perspective view illustrating a portion of memory array with ultra-small resistive elements.~~

~~FIG. 16 is a general process flow diagram to make memory element with ultra-small resistive elements.~~

DETAILED DESCRIPTION OF THE INVENTION

012 **FIG. 1** is a cross sectional view of PMCM memory with multiple solid electrolyte elements. ~~illustrating a phase-change memory element structure with ultra-small resistive elements.~~ Basically, the memory element comprises of 4 ~~(3)~~ layers: electrode layers **20** and **40**, and resistive element layer **30** and metallic layer 37. ~~The resistive layer contains a plurality of extra-small resistive elements 35.~~

~~The top surface and bottom surface of resistive element contacts with the electrode 20 and 40, and thus a single resistive element constitutes a resistor. The total resistance of all resistors basically determines the resistance value of a single memory element. The resistive layer 30 is a layer where some solid electrolyte elements 36 with size of about 1 nm to several tens nm ($1\text{ nm}=10^{-9}\text{ m}$) embedded uniformly in a high resistance matrix 32. The electrode layers 20 and 40 are made of conductive material. The whole memory cell is located between the address lines 10 and 50.~~

013 ~~The electrode layers 20 and 40 are made of conductive material. The material of electrodes layer 20 and 40 should be chosen such that this material is not mixable with resistive layer materials, i.e., resistive element 35 and matrix layer 32. So the layer contacting with the resistive element 35 also functions as a barrier layer to prevent the atoms of the resistive element 35 and 32 from diffusion into the adjacent layers 20 and 40 and the atoms of the electrode layers 20 and 40 from diffusion to resistive layer 35 and 32. For the phase change memory, since the information is stored by changing the resistance~~

~~of the resistive element 35 through the heating by the programming pulse current, the material of the electrode layers 20 and 40 is preferred, but not limited to be the some high melting temperature metal, alloy or conductive compound such as carbide and nitride, for example, WC, TiN. The electrodes 20 and 40 can also be made by the multi-layer thin film. In this case, the layer adjacent to the resistive layer 30 should also function as a barrier layer to prevent the diffusion of the atoms.~~

014 ~~The resistive element 35 is made by filling the phase change material~~ The solid electrolyte elements 36 are made by filling the solid electrolyte material into an opening of the resistive layer 30. To make the openings
~~opening,~~ a composite-phase thin film 30 is first deposited on the first or bottom electrode layer 20, ~~as shown in FIG. 2.~~ The composite-phase thin film is a layer where one phase forms the ultra-small particles 31 and embedded uniformly in another phase which forms a matrix layer 32, as shown in **FIG. 2 (3)**. The thickness of composite-phase layer is in the range of about 1 nm to 100 nm.

015 The selection of the materials for the composite-phase thin film layer should meet following requirements:

(a) the matrix layer material should be selected from a group of high resistive material so that programming current can mainly flow through the resistive elements; (b) the nano-dot particle material and matrix material are not mixable. It means that they are not soluble to each other and don't form an alloy when they come together by some means such as co-deposition of these two materials onto a ~~the same~~ substrate; (c) nano-dot particle and high resistive matrix materials are chosen such that nano-dot particle is active chemically, while the high resistive matrix material is inactive chemically to some chemical or chemical solution. So the nano-dot particle can be etched away by the selected chemicals in the later process.

016 It is easy to find the materials meeting the above requirements. The oxide, nitride, boride, carbide, boron, silicon, carbon, carboxynitride and mixture of these materials are the good candidates for high resistive matrix material, while most metals and alloys are the good candidates for the nano-dot particle material. For example, Fe/SiO₂ is a good combination of these materials. Fe is conductive material, while SiO₂ is a high resistive material. Fe and SiO₂ are not mixable. When Fe and SiO₂ were co-deposited onto a substrate by some means such as

sputtering, Fe forms very small particles which are uniformly embedded in the SiO_2 matrix layer under the certain deposition conditions. The SiO_2 is a very stable compound to most of chemicals such as acids, e.g. HCl, while Fe is active to most of acids, e.g. HCl. Since the Fe is active to HCl, while the SiO_2 is inactive to HCl, so the HCl is a suitable chemical solution to etch Fe particle and form an opening in SiO_2 matrix layer.

017 The size of the nano-dot particle is defined herein as the diameter of the particles, or their "characteristic dimension" which is equivalent to the diameter where the particles are not cylindrically shaped. The nano-dot particle size is about 1 nm to several tens nm, and more preferably of 3 nm to 50 nm.

~~018 Since the resistive element made by the method of present invention can be as small as in the nanometer scale, an extremely low energy can heat a resistive element to a very high temperature. Therefore, for the phase-change memory, the resistive element material is not necessary to be limited to some low melting temperature materials such as chalcogenide semiconductors. Some metals or alloys may be also used as resistive element material. For example,~~

~~for a 5×5×5 nm nano-dot Cr particle, a 10 nanosecond current pulse of about 5.0×10^{-2} mA can heat this particle to its melting temperature, i.e., 1890°C. The energy to melt this Cr particle is about 10^{-16} Joule, an extremely low energy. The resistance value of the Cr with size 5×5×5 nm in crystalline state is about 26 Ohms.~~

019 The composite-phase layer with nano-dot particles can be made by various thin film deposition methods such as sputtering, laser ablation, evaporation, or the chemical vapor deposition (CVD). The preferred and simple method is to co-sputter a composite target containing these two materials by the magnetron sputtering, RF sputtering or ion beam sputtering. By optimizing the deposition conditions and selecting suitable materials, a well-defined nano-dot particle **31** with desired size can be formed and embedded uniformly in the high resistive matrix layer **32**. The ~~composite-phase layer can also be made by the multi-layer thin film deposition of nano-dot particle material and matrix material. In this case, a several angstroms of high resistive matrix material and nano-dot particle material are deposited alternatively. After deposition, an anneal process maybe is necessary to form a composite phase layer~~

~~with well-defined nano-dot particles.~~ To ensure the nano-dot particles are isolated by matrix material, the volume ratio of nano-dot material and matrix material in composite-phase layer should be less than about 3/1, typically, in the range of about 1/1~1/100.

018 After forming the composite-phase layer, the nano-dot particles **31** are etched by choosing suitable chemicals. The etching process can be wet etching or dry etching. The dry etching means that the particles are etched by the plasma of some chemicals. The etching process doesn't etch the matrix. So after the particle was etched away completely, an opening **34** is formed and has the same size and shape similar (close) to the particle **31**, as shown in **FIG. 4**. After the nano-dot particles **31** are etched, the surface of the bottom electrode **20** is exposed so that the resistive element **36** ~~(35)~~ can form a good electrical contact with the electrode **20** when it is filled in the opening **34**.

019 After forming the openings **34** in the resistive layer **30**, ~~position of the nano-dot particles, the resistive element materials such as phase change material or the~~ solid electrolyte material ~~can be~~ is filled in the

openings, as shown in **FIG. 4**. A recession of the electrolyte resistive element **36** from the surface of the matrix or resistive layer may be desired and can be realized by ion mill with ion beam perpendicular to the matrix surface. Most high resistive materials such as oxide, nitride has much smaller etching rate than the most electrolyte materials. So after ion mill, a recession will be formed for electrolyte resistive element and is shown in **FIG. 5**. After forming electrolyte element **30**, a thin layer of metal **37** and upper electrode **40** are deposited on the resistive element layer **30**, as shown in **FIG. 1**. ~~to form an ultra-small resistive element. The filling of the resistive element material in the openings can be accomplished by the thin film deposition or the plating. For the thin film deposition, the resistive material will fill in the openings and also cover the surface of the matrix layer, as shown in **FIG. 5**. An ion mill process with some incident angle with the matrix layer surface can be used to mill away the resistive element material over the surface of the matrix layer, while the resistive element material inside the opening is still remained after the ion mill due to the shadowing effect, as shown in **FIG. 6**. **FIG. 7** shows the phase-change memory element structure after the ion mill.~~

020 The solid electrolyte layer 30 can also be made by
direct co-deposition of a solid electrolyte material and a
dielectric material. The solid electrolyte and dielectric
should be selected such that they are not mixable when co-
deposited together. In such a case, the solid electrolyte
material may form small cylinder embedded in the dielectric
material in some deposition conditions. ~~For the PMCM~~
~~memory, after forming the opening 34 in the resistive layer~~
~~30, the electrolyte material is filled in the opening. As~~
~~same as phase-change memory, electrolyte resistive element~~
~~can be planerized by the ion mill with incident angle and~~
~~is shown in FIG. 8. Then a recession of the electrolyte~~
~~resistive element 36 from the surface of the matrix layer~~
~~may be necessary and it can be realized by ion mill with~~
~~ion beam perpendicular to the matrix surface, as shown in~~
~~FIG. 9. Most high resistive materials such as oxide,~~
~~nitride has much smaller etching rate than the most metals.~~
~~So after ion mill, a recession will be formed for~~
~~electrolyte resistive element and is shown in FIG. 10.~~
~~After forming electrolyte element, a layer of metal 37 is~~
~~deposited on the resistive element layer 30, as shown in~~
~~FIG. 11.~~

021 After forming the resistive layer 30 for the phase-change memory or after forming metallic layer 37 for the PMCM memory, the second electrode 40 was formed on the resistive layer 30, as seen in FIG. 1, or on the metal layer 37 for the PMCM memory, as seen in FIG. 12.

022 The resistance of the memory element can be changed by using a lamination of resistive layer and conductive layer. A phase-change memory element structure with lamination of resistive layer and conductive layer is shown in FIG. 13. The selection role for the conductive 60 is the same as electrode layers 20 and 40. The advantages of laminated resistive layer memory element are improved uniformity of the resistance of each memory element and to obtain a desired resistance value. These advantages are especially of importance when the memory element size becomes substantially smaller for the extra-high density memory. Since the number of the resistive elements 35 in a single layer decreases with the memory element size if the size of the resistive element is constant. The less is the number of the resistive elements, the poorer is the uniformity of the resistance of the memory element. For example, if there is only one resistive element in single resistive layer, the resistance of each memory element may

~~change with the size of the resistive element since the there is some variation in resistive element size. So it is necessary to have certain number of the resistive elements 34 in a single memory to ensure a uniform resistance distribution among the memory elements. As same as phase-change memory, by repeating the resistive layer 30, metallic layer 37 and conductor layer 60, we can also make PMCm memory with lamination of resistive layer and conductor layer, as shown in FIG. 14.~~

023 ~~As any conventional memory element, the present memory elements including the phase-change memory or PMCm memory can be incorporated into the construction of very dense two-dimensional and three-dimensional memory arrays. FIG. 15 shows a portion of two-dimensional memory array with extra-small resistive elements. The memory element including a ultra-small resistive layer 30 and electrode layer 20 and 40 is sandwiched between the address lines. Here we define the bottom address line as X address line and top address line as Y address line.~~

024 ~~A general procedure of fabricating the present memory elements is showed in FIG. 16. To better control the processes, it is preferred that the whole memory element~~

~~layer stack including electrodes and resistive element be finished in a multi-function system with sputtering, ion mill and plasma dry etching. After forming the X address lines 10, the first electrode and composite phase layer were deposited. And then the composite phase layer was etched by the plasma. The etching process only etches the nano-dot particles. After etching, ultra-small openings were formed. And then the resistive element material was filled in the openings by the method of thin film deposition. After milling away resistive element material over the matrix layer or forming the thin metallic layer for PMCM memory, the second electrode layer 40 is formed on the resistive layer.~~

025 — ~~After forming all memory layer stack including electrodes, resistive element layers on a substrate, the layer stack then can be patterned by the conventional methods of photolithography and etching processes. To obtain an approximate square memory element, the layer stack needs to be patterned in X direction and Y direction, i.e., first forming a stripe in X direction and then forming an approximately square memory element by patterning in Y direction. An insulator should be filled in the spacing between the memory elements in the X and Y~~

~~directions. After forming the memory element, the Y address lines 50 are built on the memory elements. Although not shown here, as conventional memories, some circuits need to be accomplished before and after fabricating memory elements to isolate the each memory element for reading and writing.~~

ABSTRACT

~~The memory elements with ultra-small resistive element are fabricated by filling the resistive element material in a nano-size opening. To make nano-size opening, a layer of composite-phase thin film is formed where a phase forms nano-size particles and embedded in another phase which forms a matrix layer. Then the nano-size opening was formed by etching the nano-size particles.~~ PCMm memory with a plurality of ultra-small solid electrolyte elements was disclosed. To make ultra-small solid electrolyte elements, a layer of composite-phase thin film is formed where a phase forms nano-size particles and embedded in another phase which forms a matrix layer. Then the nano-size opening was formed by etching the nano-size particles. Ultra-small solid electrolyte elements can also be made by co-deposition of unmixable dielectric and electrolyte materials.